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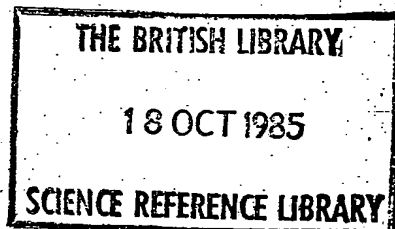
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Process for the preparation of novel acrylic
monomers and polymers.



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The following specification describes the nature of this invention.

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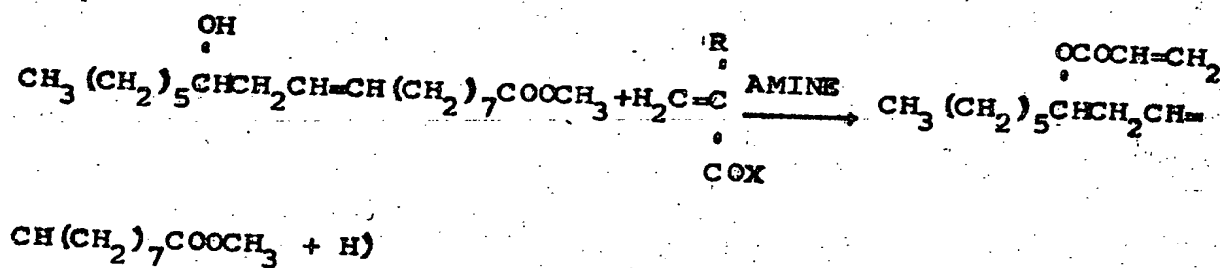
The present invention relates to a process for preparing novel acrylic and methacrylic monomers from methyl ricinoleate and their polymerisation in bulk, solution and emulsion into novel polymers.

12 acrylomethyl oleate or 12 methacrylomethyl oleate (which are the scientific names for the acrylic and methacrylic derivatives of methyl ricinoleate) can be synthesised by one of two methods.

- (1) Methyl ricinoleate is reacted with the acid halide of acrylic or methacrylic acid in the presence of an amine such as triethylamine.

The equation 1 is shown below:

EQUATION 1



where R is H or CH₃

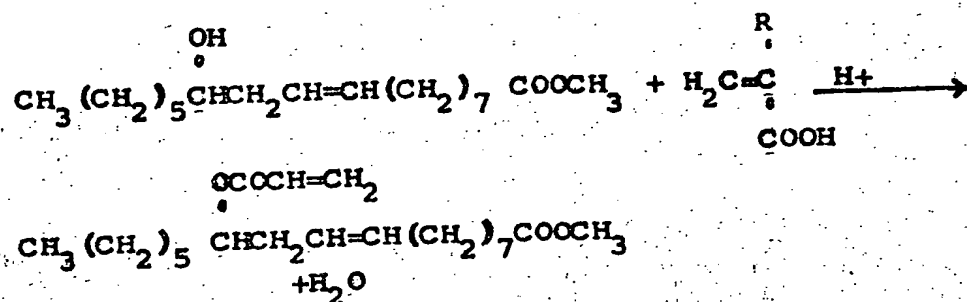
X is Cl or Br or I

The acid halide HX formed in the reaction forms a complex with the amine, which can be easily isolated by filtration and the amine can be subsequently regenerated.

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- (11) Methyl ricinoleate is reacted with acrylic or methacrylic acid in the presence of a trace of mineral acid such as sulphuric. The equation 2 is shown below:

EQUATION 2



where R is H or CH₃

The 12 acrylo methyl oleate or 12 methacrylomethyl oleate synthesised according to the process of the present invention can be further homopolymerised or copolymerised with suitable monomers in bulk, solution or emulsion to give products which might find applications in the costings, paints and adhesives industries.

According to the invention, the monomer synthesis is exemplified as follows:

Example 1

50 parts by weight of methyl ricinoleate was mixed with 200 parts by weight of chloroform and to this was simultaneously added dropwise 15 parts by weight of acrylyl chloride in chloroform and 40 parts by weight of triethylamine. The reaction

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mixture was heated to 60° for 1½ hours and then was stirred magnetically at room temperature. After 24 hours at petroleum was added to precipitate the excess triethylamine, and the solution filtered, and worked up with base. The product obtained was then distilled to give a pure product.

Example 2

30 parts by weight of methyl ricinoleate was refluxed together with 8 parts by weight of methacrylic acid in the presence of three drops (0.2ml) of concentrated sulphuric acid for four hours. Two parts by weight of hydroquinone is present to prevent homopolymerisation of methacrylic acid.

The reaction product was worked up with base, and distilled to give a pure product.

Polymerisation Studies

Emulsion homopolymerisation or copolymerisation of the above monomers with common vinyl monomers such as methyl methacrylate, styrene or vinyl acetate was carried out with a water solution free radical initiator at 80°C for 4 hours.

Solution polymerisation of the above monomers was carried out in the usual organic solvents such as ethyl acetate, ethanol, acetone at 50 - 75°C with a free radical initiator.

Example 3

Solution Copolymerisation

50 parts by weight of 12 acrylomethylolate and 50 parts by weight of methyricinoleate in 150 parts by weight of ethyl

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acetate and 0.5 parts by weight of 22' azobisisobutyronitrile were heated together for 3 hours at 75°C to give a solution copolymer of molecular weight of around 40,000.

Example 4

Emulsion Copolymerisation:

300 parts by weight of water were taken and to it 0.3 parts by weight of NaCl, 0.624 parts by weight of Carboxy methyl cellulose, 0.45 parts by weight of sodium pentachloro-cophenate, and 0.871 parts by weight of the nonionic detergent were added. The mixture was stirred at 85°C for 30 minutes.

50 parts by weight of 12 acrylo methyl oleate and 50 parts by weight of methyl Methacrylate were mixed together and to it 0.2 parts by weight of Anionic detergent, 5.129 gms. of nonionic detergent were added (I) 3.8 parts by weight of potassium persulfate were dissolved in 30 parts by weight of water (II) 10% of I and II are added to the original mixture, as seeding stage monomer mixture. The resulting mixture is stirred for 10 minutes at 85°C and then the rest of the monomer mixture along with the initiator solution is added dropwise. When the addition is over the mixture is stirred at 90°C for 30 minutes more.

Dated this 14th day of July, 1980.

A. V. Nathan
(A.V. NATHAN)
OF REMFERY & SON
AGENT FOR THE APPLICANTS

~~154467~~
COMPLETE SPECIFICATION
(Section-10)

Process for the preparation of novel acrylic monomers and polymers.

The Alkali and Chemical Corporation of India Limited, an Indian Company, of ICI House, 34 Chowringhee Road, Calcutta-700 071, West Bengal, India.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

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This invention is conceived by DR. ANNOOTTAM GHOSH.

The present invention relates to a process for preparing novel acrylic monomers of methyl esters of ricinoleic acid or of mixed fatty acids of castor oil which is predominantly ricinoleic acid, ~~and their~~ *which novel monomers are easily amenable to* subsequent polymerisation in bulk, solution and emulsion.

These monomers and the polymers derived from ricinoleic acid or mixed fatty acids of castor oil are entirely novel compounds and have great versatility particularly in regard to applications in surface coatings industry.

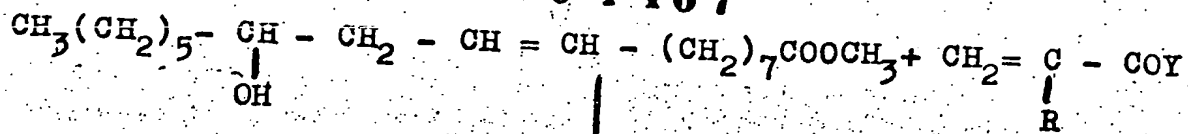
According to the invention there is provided a process for preparing novel acrylic monomers of methyl esters of ricinoleic acid or mixed fatty acids of castor oil which comprises reacting the said methyl esters with an acrylic acid or derivative thereof of the formula
$$\text{CH}_2 = \underset{\substack{| \\ \text{R}}}{\text{C}} - \text{COX},$$
 where R is H or CH_3 and X is Br or Cl, in the presence of an amine.

~~The invention also provides a process for the polymerisation of the novel acrylic polymers.~~

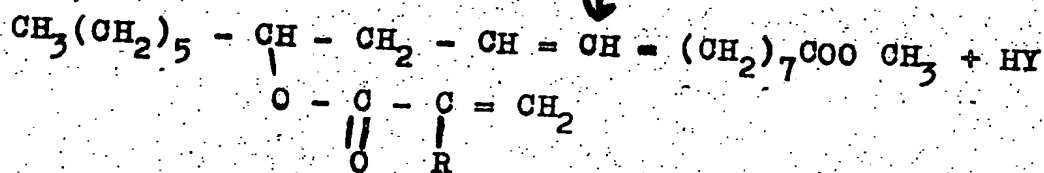
The reaction with methyl esters of mixed fatty acids of castor oil is illustrated below:

Where an acrylic acid derivative being an acid chloride or bromide is used as the reactant:

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Primary amine



where Y is Cl or Br and R is H or CH₃.

The acid formed in the reaction forms a complex with the amine, which is easily isolated by filtration and the amine can be regenerated and reused. A suitable amine is triethylamine.

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Where methyl esters of mixed fatty acids of castor oil are used, similar reaction takes place with the methyl ricinoleate present in such ester mixtures other fatty acid esters present in the mixture remaining basically unaffected.

"The novel monomers according to the process of the present invention can be further homopolymerized or copolymerized with suitable monomers in bulk, solution or emulsion to give products which might find applications in coatings, paints and adhesive industries. The low molecular weight solution copolymers may be used as adhesives and the high molecular weight emulsion copolymers as vehicles for paints.

According to the invention, the monomer preparation is exemplified as below. In these examples the scientific names, viz. 12-acrylo methyl oleate or 12-methacrylo methyl oleate, have been used to designate the novel monomer.

E X A M P L E - I

50 parts by weight of methyl ricinoleate was mixed with 200 parts by weight of chloroform and to this was added dropwise, 15 parts by weight of acryloyl chloride in chloroform and 40 parts by weight of triethylamine. The reaction mixture was heated to 60°C for 1½ hours and then was stirred magnetically at room temperature. After 24 hours, petroleum ether was added to precipitate the excess of triethylamine salt and the solution was filtered and worked up with base. The solvent was then distilled off to give

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the desired product. The yield was found to be about 95% and the product characterised by infra-red spectroscopy *from the two monomers prepared*

The preparation of polymers *h* according to the invention is exemplified below:

EXAMPLE - II

Solution Copolymerisation

50 parts by weight of 12-acrylo methyl oleate and 50 parts by weight of methyl methacrylate in 150 parts by weight of ethyl acetate and 0.5 parts by weight of 2,2' azo-bis-isobutyronitrile (free radical initiator) were heated together for 3 hours at 75°C in nitrogen atmosphere to give a solution copolymer of an average molecular weight of 40,000. The conversion of monomer to polymer was 89.7%. Glass transition studies showed that the polymer displayed only one transition, confirming that it was a genuine copolymer and not a mixture of two homopolymers. The solution copolymer may be used as such or the solvent may be evaporated off to give a solid copolymer.

Similar reaction in case of 12-methacrylo methyl oleate gave a copolymer of average molecular weight of 11,000, the conversion of monomer to polymer being 83.2%.

EXAMPLE -III

4 parts by weight of 12-acrylo methyl oleate, 16 parts by weight of styrene, 0.4 parts by weight of 2,2' azo-bis-isobutyronitrile (free radical initiator) and _____

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80 parts by weight of ethyl acetate were put in a 250cc round bottom flask and the copolymerisation carried out in nitrogen atmosphere at 75°C for 5 hours.

The conversion of monomer to polymer was found to be 89.2%. The average molecular weight = 13,500.

A similar experiment was carried out with 12-methacrylo methyl oleate, which gave a copolymer having average molecular weight of 9,000 and 78.2% conversion. Glass transition studies showed that the polymer displayed only one transition, confirming that it was a genuine co-polymer and not a mixture of two homopolymers. The solution copolymer may be used as such or the solvent may be evaporated off yielding a solid copolymer.

EXAMPLE - IV

10 parts by weight of 12-methacrylo methyl oleate was copolymerised with 10 parts by weight of vinyl acetate in 80 parts by weight of ethyl acetate using 0.4 parts by weight of 2,2' azo-bis-isobutyronitrile in nitrogen atmosphere giving a copolymer of average molecular weight of 11,000, conversion of monomer to polymer of 53.4%. Glass transition studies showed that the polymer displayed only one transition confirming that a genuine copolymer had been formed and not a mixture of two homopolymers.

A similar experiment was carried out with 12-acrylo methyl oleate which gave a copolymer of molecular weight mainly 15,000 and conversion of monomer to polymer, 56.2%.

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The polymer solutions can be used as such or the solvent evaporated off to yield the solid copolymer.

EXAMPLE -- V1

Emulsion Copolymerisation

Emulsion copolymerisation of 12-methacrylo methyl oleate and other methyl esters of the mixed fatty acids present in castor oil with methyl methacrylate carried out as described below:

80 parts by weight of methyl methacrylate, 85 parts by weight of a mixture of 12-methacrylo methyl oleate and methyl esters of the mixed fatty acids of castor oil, (in this mixture about 85% is 12-methacrylo methyl oleate and the remaining 15% are the methyl esters of the other fatty acids present in castor oil), 2 parts by weight of methacrylic acid, 5 parts by weight of a non-ionic surfactant, 2 parts by weight of an anionic surfactant were mixed together. To this was added 2.0 parts by weight potassium persulphate, (initiator) and 200 parts by weight tap water containing 1 part by weight sodium carboxy methyl cellulose. The entire mixture was stirred at 220 rpm in a 500ml. round bottom flask in an atmosphere of nitrogen at 85°C. The reaction was carried out for 4 1/2 hours. The conversion of monomer to polymer was 94%. The average molecular weight was 1,15,000. Glass transition studies showed that the polymer displayed only one transition confirming that a genuine copolymer had been formed and not a mixture of two homopolymers.

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The emulsion copolymer may be used as such or the water evaporated off leaving the solid copolymer.

EXAMPLE - VI

Bulk Copolymerisation

50 parts by weight of 12-methacrylo methyl oleate, 50 parts by weight of methyl methacrylate and 0.4 parts by weight of 2,2' azo-bis-isobutyronitrile were heated to 75°C with magnetic stirring. The reaction was carried out for 4 hours giving rise to a solid. The copolymer formed gave an average molecular weight of 60,000 conversion of monomer to polymer of 63.7%. Glass transition studies were carried out and since only one transition was observed, it is indicated that a genuine copolymer had been formed and not a mixture of two homopolymers.

A similar experiment was carried out with 12-methacrylo methyl oleate which gave an average molecular weight of mainly 55,000, conversion of monomer to polymer of 61.9%.

WE CLAIM:-

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1. A process for preparing novel acrylic monomers of methyl esters of ricinoleic acid or mixed fatty acids of castor oil which comprises reacting the said methyl esters with an acrylic acid or derivative thereof of the formula $\text{CH}_2 = \underset{\text{R}}{\text{C}} - \text{COX}$, where R is H or CH_3 and X is Br or Cl, in the presence of an amine.
2. A process as claimed in claim 1 wherein the amine used is triethylamine, or any other primary amines.
3. A process for the preparation of novel acrylic monomers substantially herein described with reference to example I.

Dated this 8th day of September, 1981.

A. Gabriel

(A. GABRIEL)
OF REMFRY & SON
AGENT FOR THE APPLICANTS.

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